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Authors(s)	Horn, Sabine, Gandolfi, Claudio, Albrecht, Martin
Publication date	2011-06
Publication information	Horn, Sabine, Claudio Gandolfi, and Martin Albrecht. "Transfer Hydrogenation of Ketones and Activated Olefins Using Chelating NHC Ruthenium Complexes." Wiley, June 2011. https://doi.org/10.1002/ejic.201100143 .
Publisher	Wiley
Item record/more information	http://hdl.handle.net/10197/6570
Publisher's statement	This is the author's version of the following article: Sabine Horn, Claudio Gandolfi and Martin Albrecht (2011) "Transfer Hydrogenation of Ketones and Activated Olefins Using Chelating NHC Ruthenium Complexes" European Journal of Inorganic Chemistry, 2011(18) : 2863-2868 which has been published in final form at http://dx.doi.org/10.1002/ejic.201100143
Publisher's version (DOI)	10.1002/ejic.201100143

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Transfer Hydrogenation of Ketones and Activated Olefins Using Chelating NHC Ruthenium Complexes

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Keywords: Ruthenium / N-heterocyclic carbene / transfer hydrogenation / unsaturated ketones / chemoselectivity

N-heterocyclic carbene (NHC) ruthenium complexes comprising different donor substituents attached to the NHC ligand efficiently catalyse the transfer hydrogenation of ketones and of activated olefins in α,β -unsaturated ketones to give saturated alcohols. The most active catalyst precursor contained a tethered olefin as hemilabile donor site. This complex also converts nitriles and depending on the reaction conditions, either benzylamines are

produced via transfer hydrogenation, or amides from formal addition of H₂O. Kinetic analysis of the double hydrogenation of α,β -unsaturated ketones indicates fast isomerisation of the enol intermediate to its saturated ketone tautomer prior to the second hydrogenation.

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Introduction

Catalytic C–H bond making and breaking is one of the most useful synthetic application of organometallic chemistry. In most hydrogenation^[1] and isomerisation reactions,^[2] the catalytically active species is a transition metal-hydride which is often generated *in situ*. Various strategies have been investigated to generate such reactive M–H intermediates including the oxidative addition of molecular hydrogen, C–H bond activation of a substrate and hydride abstraction from a hydrogen source such as a primary or secondary alcohol, amine, or formic acid.^[3] This latter method, *viz.* the abstraction of hydrogen from a donor molecule, constitutes a key step of transfer hydrogenation,^[4] an alternative approach to direct hydrogenation which avoids the use of hazardous H₂ gas.

Recently, we have shown that Ru(arene) complexes containing a bidentate chelating N-heterocyclic carbene (NHC) ligand are effective catalyst precursors for the direct hydrogenation of olefins using H₂ (complexes 1–4, Figure 1).^[5] The chelating group in these complexes has a pronounced effect on the catalytic activity and the stability of the complex. While the olefin donor group in 1 was rapidly hydrogenated, thus inducing complex decomposition and predominantly heterogeneous hydrogenation, the carboxylate group in 2 markedly increased the stability of the complex. Owing to the presence of the carboxylate group, both homolytic dihydrogen activation, typically *via* oxidative addition and RuH₂ formation, or heterolytic dihydrogen cleavage across the Ru–O bond may be surmised. Heterolytic cleavage and involvement of a ruthenium monohydride intermediate should be facilitated if the source of dihydrogen is strongly polarised. For example in *i*-PrOH, hydrogen is formally provided through a proton, bound to oxygen, and a hydride-like carbinol hydrogen.^[4] Based on this hypothesis and considering the privileged role of Ru(arene) scaffolds in (transfer) hydrogenation,^[3b,c,6] and specifically the success of the corresponding NHC-containing complexes in hydrogen transfer

reactions,^[7] we became interested to probe the activity of complexes 1–4 in the transfer hydrogenation. A particularly intriguing aspect was the possibility to use a single complex for either direct or transfer hydrogenation of substrates. Despite the conceptual analogy of these two hydrogenation processes, only few systems are known that exhibit such dual activity.^[8]

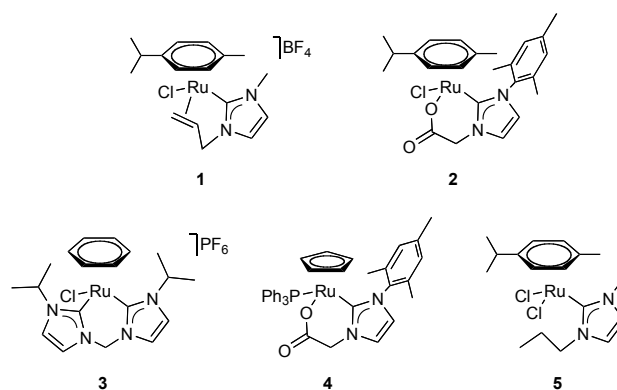


Figure 1. Chelating (NHC) ruthenium complexes 1–4 and monodentate carbene ruthenium complex 5.

Results and Discussion

Transfer hydrogenation of ketones. Preliminary tests concentrated on evaluating the transfer hydrogenation activity of complexes 1–4 by using benzophenone as a model ketone. Standard transfer hydrogenation conditions were used,^[4] *viz.* refluxing *i*-PrOH as hydrogen source and KOH as activator (substrate/base/complex 100:10:1; Table 1). Distinct differences in catalytic hydrogen transfer activities were observed for these complexes. While complete conversion was reached with all complexes apart from 4 after extended reaction times, complex 1 was most active (> 90% after 5 h). Using a carboxylate tether as in complex 2 decreased the conversion to 75% and an even lower conversion (63%) was noted after 5 h with the dicarbene complex 3. Changing the Ru(arene)Cl scaffold in complex 2 to a Ru(Cp)PPh₃ fragment was disadvantageous and complex 4 comprising the same carboxylate-functionalised NHC ligand as 2

displayed poor activity, reaching a modest 32% conversion after 24 h.

Table 1. Catalytic transfer hydrogenation of benzophenone.^[a]

entry	catalyst	chelating group	conversion (time)	
1	1	olefin	90% (5 h)	98% (24 h)
2	2	COO ⁻	75% (5 h)	98% (24 h)
3	3	NHC	63% (5 h)	98% (24 h)
4	4	COO ⁻	9% (5 h)	32% (24 h)
5 ^[b]	1	olefin	59% (10 min)	96% (30 min)
6 ^[b]	5	(Cl ⁻)	36% (10 min)	63% (30 min)
7 ^[b]	5 + AgBF ₄	(solvent)	59% (10 min)	79% (30 min)

[a] General conditions: substrate/KOH/catalyst 100:10:1, conversions determined by ¹H NMR spectroscopy or GC-MS analysis. [b] in sealed Schlenk tube with degassed solvent.

The reaction conditions were further optimised for complex **1** showing the highest activity. The hydrogen transfer rate increased substantially upon degassing the solvent and upon performing the reaction in a gas-tight tube under inert atmosphere and at 90 °C. Under these conditions, complete conversion was reached after less than one hour (Table 1 entry 5). No induction time was noted. After 10 min, 59% conversion was achieved, which corresponds to an approximate turnover frequency at 50% conversion TOF₅₀ ~ 360 h⁻¹. This rate is competitive with other recently reported ruthenium-carbene complexes,^[7,9] though considerably lower than the most active transfer hydrogenation catalysts, which have TOF₅₀ > 10,000 h⁻¹.^[10]

Since hydrogenation of the olefinic tether may constitute a potential catalyst (de)activation,^[11] complex **5** comprising an *n*-propyl wingtip group was investigated as the saturated version of **1** (*cf* Scheme 1). Complex **5** was synthesised by a transmetalation procedure and was characterised spectroscopically as well as by X-ray diffraction (Fig. 2).^[12] The pertinent bond lengths (Ru1–C11 2.063(2) and angles are within expectation.^[13] Under identical reaction conditions, complex **5** was a considerably less active hydrogen transfer catalyst, achieving 36% conversion after 10 min (Table 1, entry 6). This performance corresponds to an estimated TOF₅₀ ~ 150 h⁻¹. Attempts to introduce a labile ligand in complex **5** in order to mimic the hemilability of the olefin donor in complex **1** improve the catalytic activity. For example, reaction of complex **5** with AgBF₄ allowed for substitution of a ruthenium-bound chloride in **5** by a solvent molecule and an essentially non-coordinating anion. The resulting complex showed an initial activity in transfer hydrogenation that compares well to that of complex **1** (entry 7), though completion is not reached within 30 min. Functionalisation of the ruthenium-carbene unit with an olefinic donor group seems to impart a proper balance of lability, entailing swift activation of the catalyst precursor, and stability of the catalytic resting states towards undesired decomposition. These studies thus underline the relevance of donor stabilisation as a concept in NHC transition metal catalysis.^[14]

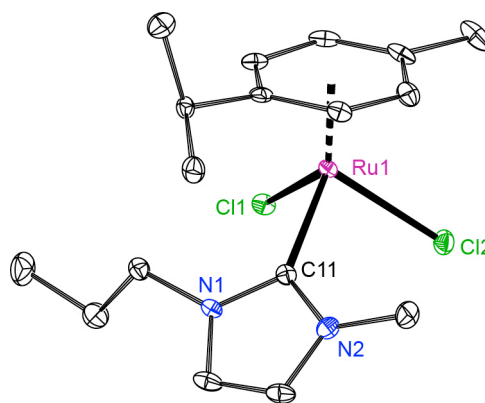


Figure 2. ORTEP representation of complex **5** (50% probability ellipsoids, hydrogen atoms, co-crystallised CH₂Cl₂, and the second crystallographically independent complex molecule omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru1–C11 2.063(2), Ru1–C11 2.4297(6), Ru1–Cl2 2.4437(6), C11–Ru1–C11 88.83(7), C11–Ru1–Cl2 88.68(7), C11–Ru1–Cl2 85.15(2).

The appreciable catalytic activity of complex **1** strongly suggests that the crucial ruthenium hydride intermediate is not only accessible under direct hydrogenation conditions, but also *via* transfer hydrogenation.^[15] We therefore extended our studies to the hydrogenation of other functional groups and activated C=C bonds, which were successfully converted by direct hydrogenation using complexes **1–4**.^[5]

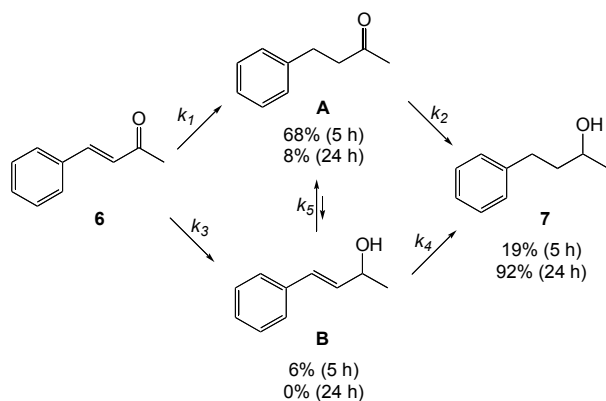
Transfer hydrogenation of other functional groups and activated olefins. Transfer hydrogenation of esters, nitro, and amine groups met limited success (Table 2). The ester group in methylbenzoate appeared to be unreactive and the conversion to benzoic acid most likely ensued from saponification due to the presence of aqueous KOH as additive. Only low activity was noted for the transfer hydrogenation of nitrobenzene to aniline. With benzonitrile, however, clean formation of benzamide occurred. Although this reaction typically requires a large excess of H₂O to achieve substantial conversions,^[16] complex **1** gave quantitative products after 24 h in the presence of only 2.5 molequiv. H₂O relative to the substrate. Hydrogenation of benzonitrile to benzylamine was not observed under these conditions.^[17] When aqueous KOH was replaced by anhydrous *t*-BuOK, transfer hydrogenation to benzylamine took place, albeit only in low yields.

Table 2. Catalytic transfer hydrogenation of functional groups.^[a]

substrate	product	conversion
		15%
		7%
		97%
		13% ^[b]

[a] General conditions as in Table 1 using complex **1** as catalyst precursor and degassed solvents in sealed vessels; conversions after 24 h. [b] *t*-BuOK instead of aq. KOH.

Transfer hydrogenation has been widely used to reduce carbonyl functions, but also C=C double bonds conjugated to an electron-withdrawing group such as a carbonyl, ester, acid, nitro, or a cyano group.^[18] Hence, complex **1** was tested in the transfer hydrogenation of the α,β -unsaturated ketone **6** as an activated olefin. Under optimised reaction conditions, double transfer hydrogenation to 4-phenylbutan-2-ol (**7**) took place (91% after 5 h, Scheme 1). This product selectivity is in contrast to a study using a close analogue of complex **5**, which revealed predominant formation of the ketone **A**.^[7b]



Scheme 1. Transfer hydrogenation of benzylideneacetone (**6**) rate constants k refer to observed rate constants k_{obs} .

In an attempt to investigate the pathway of the enone reduction in more detail transfer hydrogenation was performed in air to deliberately decelerate the catalyst activity (*i.e.* unoptimised conditions, Table 1). Time-dependent monitoring of the reaction using GC-MS analysis and ^1H NMR spectroscopy consistently revealed the presence of the monohydrogenated ketone **A** as prevailing intermediate, indicated by the diagnostic multiplets at δ_{H} 2.9 and 2.75 and the singlet at δ_{H} 2.15. Additionally, enol **B** was detected as a minor component at an early stage of the reaction.

A time profile of the reaction is depicted in Figure 3. Accordingly, intermediate **A** reached a maximum concentration of 68% after 5 h reaction time. After 24 h, the starting material and intermediate **B** were completely consumed, and the fully hydrogenated alcohol **7** was the major product along with trace residues of **A** (8%). While some catalysts have been reported to be inactive in converting the enol intermediate **B** and to yield mixtures,^[18c,19] the catalyst derived from **1** is active towards both intermediates **A** and **B**.^[20]

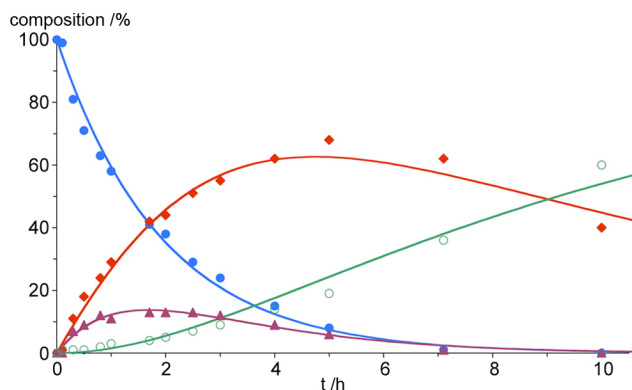


Figure 3. Time-dependent monitoring of the transfer hydrogenation of **6** (●) by GC-MS and evolution of products **A** (◆), **B** (▲), and **7** (○). Solid

lines correspond to fitted rate constants using Berkeley Madonna upon suppressing direct hydrogenation of the enol intermediate **B** to **7**.

The activity profile suggests that both intermediates **A** and **B** are suitable substrates for a second transfer hydrogenation or, alternatively, that isomerisation between the two intermediates occurs and one substrate is preferentially hydrogenated.^[21] The latter model may be supported by the fact that the rate for the formation of **A** is comparable to that of benzophenone hydrogenation (Table 1), thus insinuating a direct formation of **A** from **6**. Intermediate **A** may be further accumulated *via* keto-enol isomerisation from enol **B** with an equilibrium constant that seems to largely favour the keto isomer.^[2] The reaction profile would be expected to be similar also in the former model, assuming that formation of **A** is favored over the formation of **B** to such an extent that, in combination with faster hydrogenation of **B** than **A** to the final product, the enol intermediate concentration falls below detection limits after some time. Kinetic modelling was therefore used to shed further light on this double transfer hydrogenation process. Taking into account the considerations outlined above, two different hypotheses were tested using the Berkeley Madonna software.^[22] In the first one, isomerisation between intermediates **A** and **B** was considered to be negligible ($k_5 = 0$ in Scheme 1),^[23] implying that intermediates **A** and **B** were hydrogenated directly to the saturated product **7**. In the second model, isomerisation was enforced and instead, hydrogenation of the C=C bond in intermediate **B** was discarded ($k_4 = 0$), *i.e.* all enol intermediate isomerises to the anone species prior to the second transfer hydrogenation step. Only the second model succeeded in appropriately reproducing the time-dependent concentrations of all four components during the reaction (Figure 3). Upon suppressing the isomerisation process, only the concentrations for starting material and the final product were simulated properly while the intermediates showed a poor match with the observed data.^[24]

Based on the best fitting kinetic model, the rate constants for the hydrogenation of the keto functionality is only slightly faster than that of the conjugated olefin ($k_1 = 0.299$, $k_3 = 0.222$). Transfer hydrogenation of the ketone in **A** is, however, substantially slower ($k_2 = 0.108$) than in the conjugated system (*viz.* k_3 , formation of **B** from **6**). By far the fastest process is the isomerisation of the enol **B** into the anone intermediate **A** ($k_5 = 0.672$). Different mechanisms have been proposed for this enol-to-ketone isomerisation,^[2] including transient hydrogenation (reductive process), transient dehydrogenation (oxidative process), and direct isomerisation (probably *via* an allylic intermediate). The former two processes seem unlikely in the system studied here since the reaction conditions strongly disfavour transfer dehydrogenation. The oxidative process would involve here the rebuilding of **6**, which is not competitive to the oxidation of *i*-PrOH, which is present in large excess as a solvent.

In line with the kinetic model, transfer hydrogenation of 4-*t*-butylstyrene as a non-isomerisable analogue of intermediate **B** proceeded sluggishly. A moderate conversion of 18% was accomplished after 24 h with complex **1** as the catalyst precursor. While a remarkable TOF of 10 h^{-1} was noted for the first 30 min, the overall reaction rate is much too low to account for a direct hydrogenation of intermediate **B** without prior isomerisation to the ketone **A**. Apparently, the electron-withdrawing nature of the phenyl substituent in styryl derivatives does not sufficiently polarise the olefinic C=C bond. The lower catalytic activity of **1** towards styrene as compared to **6** may also suggest a critical role of the oxygen lone pair for the formation of a classical η^3 -allyl or a η^3 -oxoallyl intermediate.^[25]

Conclusions

We have demonstrated that ruthenium NHC complexes that have previously shown activity in catalysing direct hydrogenation and the activation of H₂ are also efficient catalysts for the transfer hydrogenation of ketones. Depending on the reaction conditions, nitriles and α,β -unsaturated ketones were successfully converted as well. Kinetic analysis of the enone reduction suggests that the ruthenium NHC complexes are not only catalysing transfer hydrogenation but also induce a rapid keto-enol tautomerisation. Such isomerisations may become useful for H/D exchange reactions and also for the transfer hydrogenation of less activated substrates. Expansion of our results in these directions is currently in progress.

Experimental Section

General. The preparation of complexes **1–4**^[5] and 1-propyl-3-methylimidazolium bromide^[26] was reported previously. CH₂Cl₂ was dried over P₂O₅ and distilled before use. Anhydrous *i*-PrOH was purchased in 99.5% purity and used without further treatment. All other reagents were commercially available and were used as received. Column chromatography was carried out on Apollo Scientific ZEOprep 60 (40–63 microns). All ¹H NMR spectra were recorded at 25 °C on Bruker or Varian spectrometers and referenced to residual protio solvent signals (δ in ppm, *J* in Hz). High resolution mass spectrometry was carried out with a Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray source. GC-MS analyses were performed on a GCT Premier GC-MS (Micromass/Waters Corp. USA) using a temperature gradient.

Synthesis of Complex 5. A suspension of 1-propyl-3-methylimidazolium bromide (270 mg, 1.32 mmol) in CH₂Cl₂ (10 mL) was placed under N₂ atmosphere, and degassed *via* 3 freeze-pump-thaw cycles. Ag₂O (153 mg, 0.66 mmol) was added and the reaction mixture was stirred in the dark for 16 h. The crude product was filtered through a pad of Celite. The filtrate was concentrated to 5 mL and added to a solution of [RuCl₂(η^6 -*p*-cymene)]₂ (404 mg, 0.66 mmol) in degassed CH₂Cl₂ (10 mL). A solid formed immediately and the reaction mixture was stirred for 4 h in the dark. After filtration through Celite and evaporation of all volatiles, the crude product was purified by column chromatography on silica (CH₃CN/H₂O 10:1) and recrystallisation from CH₂Cl₂/C₅H₁₂ to afford complex **5** as red crystals (155 mg, 27%). ¹H NMR (acetone-*D*₆, 500 MHz, 25 °C): δ 0.94 (t, ³*J*_{HH} = 7.4 Hz, 3H, NCH₂CH₂CH₃), 1.29 (d, ³*J*_{HH} = 6.9 Hz, 6H, CH(CH₃)₂), 1.84 (m, 2H, NCH₂CH₂CH₃), 1.96 (s, 3H, C_{cym}-CH₃), 2.97 (sept, ³*J*_{HH} = 6.9 Hz, 1H, CHMe₂), 4.00 (s, 3H, NCH₃), 4.32 (br, 2H, NCH₂CH₂CH₃) 5.15, 5.47 (2 × d, ³*J*_{HH} = 5.9 Hz, 2H, C_{cym}-H), 7.31, 7.37 (2 × d, ³*J*_{HH} = 2.0 Hz, 2H, C_{im}-H). ¹³C {¹H} NMR (acetone-*D*₆, 125 MHz, 25 °C): δ 11.8 (NCH₂CH₂CH₃), 19.2 (C_{cym}-CH₃), 23.2 (CH(CH₃)₂), 26.2 (NCH₂CH₂CH₃), 32.0 (CHMe₂), 40.1 (NCH₃), 53.9 (NCH₂CH₂CH₃), 82.6, 88.1 (2 × C_{cym}-H), 99.7, 109.6 (2 × C_{cym}-C), 122.9, 125.5 (2 × C_{im}-H), 175.9 (C_{im}-Ru). HRMS (ES+): calcd. for C₁₇H₂₆N₂ClRu [M - Cl]⁺ 395.0828, found 395.0837.

Typical Procedure for Catalytic Transfer Hydrogenation. The catalyst (20 μ mol) was dissolved in *i*-PrOH (10 mL).^[27] KOH (0.10 mL of 2 M solution in H₂O, 0.2 mmol) was added and the mixture was heated to reflux for 10 min. Then the substrate (2.0 mmol), containing the internal standard 3,5-dimethylanisole (0.6 mmol), was added at once. Aliquots (0.2 mL) were taken at fixed times, quenched with pentane (1 mL), and filtered through a short path of silica. The silica was washed with Et₂O (2 × 2 mL) and the combined organic filtrates were analysed by GC-MS or carefully evaporated and analysed by ¹H NMR spectroscopy.

Optimised Procedure for Catalytic Transfer Hydrogenation. A 10 mL oven-dried Schlenk-tube was placed under N₂ and charged with *i*-PrOH (10

mL). The solvent was degassed *via* 3 freeze-pump-thaw cycles and placed under N₂ again. The catalyst (20 μ mol) was added and dissolved *via* ultrasonication (10 min, 40 °C). KOH (0.1 mL, 2M in H₂O, 0.2 mmol) was added and the mixture pre-heated in a septum-sealed tube at 90 °C for 10 min. Substrate (2.0 mmol) and the internal standard 3,5-dimethylanisole (80 μ L, 0.6 mmol) were added *via* syringe. Aliquots (0.2 mL) were taken at fixed times and analysed as outlined above.

Supporting Information (see footnote on the first page of this article): Kinetic model including the transformation of **B** directly to **7** and crystallographic details.

Acknowledgments

We thank Prof. More O’Ferrall for fruitful discussions, Mr. Conboy for technical assistance, and Dr. Müller-Bunz for crystallographic analyses. This work has been financially supported by the European Research Council (ERC StG 208561).

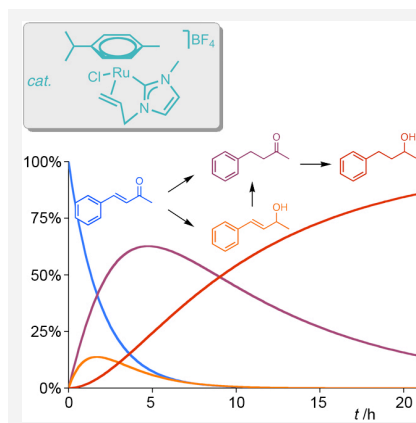
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- [23] All rate constants refer to observed rates *k*_{obs} for each step, which may be considered to be effective rate constants (apart from *k*₅) due to the large excess of *i*-PrOH, which essentially suppresses the reverse dehydrogenation reaction. An exception to this approximation is the isomerisation rate *k*₅, which presumably does not involve *i*-PrOH.
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Received: ((will be filled in by the editorial staff))
 Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents

The catalytic activity of N-heterocyclic carbene ruthenium complexes in transfer hydrogenation is strongly influenced by the donor functionality at the carbene ligand, with olefins imparting an optimal balance between lability (catalyst precursor activation) and stability (avoiding catalyst decomposition) and allow ketones and activated olefins to be transfer hydrogenated efficiently (see left).



transfer hydrogenation

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Transfer Hydrogenation of Ketones and Activated Olefins Using Chelating NHC Ruthenium Complexes

Keywords: Ruthenium / N-heterocyclic carbene / transfer hydrogenation / unsaturated ketones / chemoselectivity